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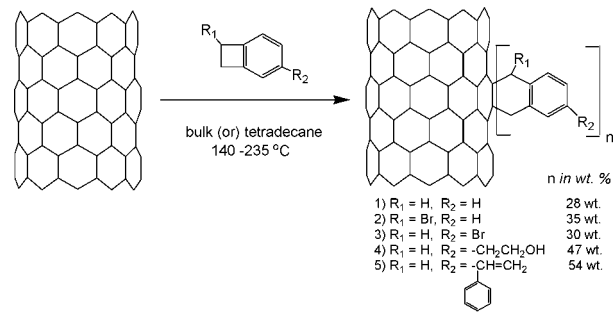
Surface modification of carbon nanotubes (CNTs) through covalent functionalization is vital for the development of high-performance composite materials, chemosensors, nanoelectronics, photovoltaic devices, as well as for a range of biomedical applications.[1] Several methods have been developed to functionalize CNTs.[2–8] The introduction of acid groups by acid digestion disrupts the structural integrity of CNTs. Apart from shortening the tubes, oxidatively generated acid groups are inhomogenously located at the tips of broken CNTs and, hence, functionalization using acid groups as precursors does not give a statistical distribution of functional groups throughout the surface of the CNTs.

The methods that have been explored for the functionalization of the sp^2 network of the CNTs include addition reactions of azomethine ylides,[3] bromomalonates,[4] diazonium salts,[5] nucleophilic carbenes,[6] nitrenes,[7] and free radicals.[8] These methods can produce a higher extent of functionalization compared to the oxidative method. Recently, the Diels–Alder reaction has been used for the functionalization of single-wall carbon nanotubes,[9–11] requiring the assistance of microwave irradiation for the functionalization of soluble SWNTs,[10] and in another case, the reaction was performed in the presence of transition metal catalyst under high-pressure.[11] Nevertheless, these reactions do not exhibit control over the degree of functionalization and require removal of the catalyst[11] and the dissolution of CNTs.[10]

Scheme 1. Diels–Alder Adduct of Various Benzocyclobutenes with Multiwalled Carbon Nanotubes



Benzocyclobutene is a class of diene which can be used in the Diels−Alder reaction with the sp^2 carbons of aromatic system through an *o*-quinodimethane intermediate.[12] The reaction of benzocyclobutene with CNTs has not been performed prior to this work, although its feasibility has been shown theoretically.[9] Here, we report a controlled functionalization of multiwalled carbon nanotubes through Diels–Alder [4 + 2] cycloaddition of various substituted benzocyclobutenes and investigate the extent of control over the functionalization, in bulk and in solution at different temperatures. The stained ring of the benzocyclobutene is susceptible to thermal ring opening to form o-quinodimethane which can undergo [4 + 2] Diels–Alder cycloaddition exclusively to 6–6 bonds of fused aromatic rings.[12] Accordingly, in an attempt to add organic moieties on the surface of CNTs, several substituted benzocyclobutenes (**1**−**5**) were reacted with multiwalled carbon nanotubes (MWNTs; Scheme 1). Benzocyclobutenes containing a hydroxyl group (**4**, BCB-CH_2CH_2OH) and 1-phenyl-1-benzocyclobutene ethylene (**5**, BCB-DPE) were synthesized from the reaction of a Grignard reagent of 4-bromobenzocyclobutene with ethylene oxide and acetophenone, respectively. Experiments were performed in bulk as well as in tetradecane. In a typical experiment, 20 mg of pristine MWNTs were reacted in bulk with 150 mg of benzocyclobutene (BCB) at different temperatures ranging from 140 to 235 °C for 24 h. In case of a reaction in tetradecane, 100 mg of MWNTs was taken in 5 mL of tetradecane and 1 mL of BCB or substituted BCB was added dropwise via a syringe pump with vigorous stirring under argon.

After the reaction, the MWNTs were collected by washing with copious amount of tetrahydrofuran (THF) and filtered using a Teflon membrane (0.2 μm pore). The washing was

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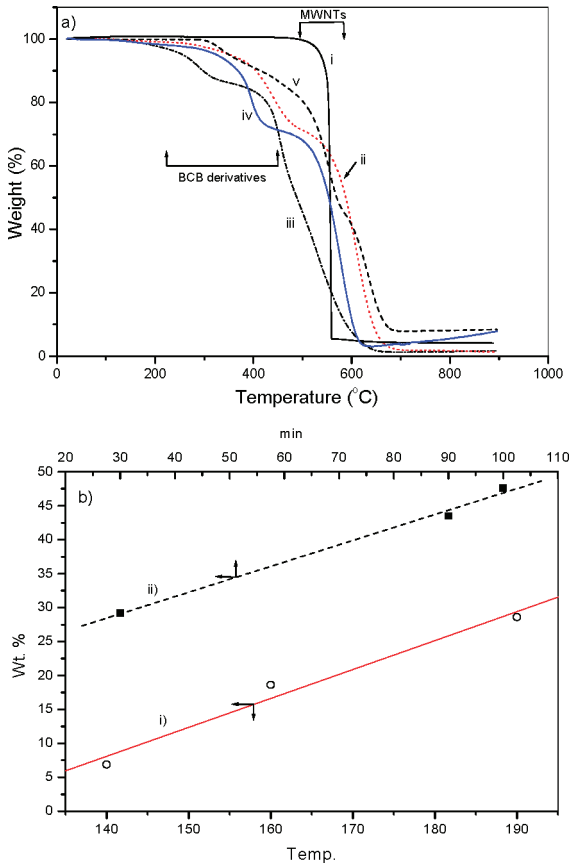

Figure 1. (a) TGA of MWNTs grafted with various derivatives of BCB: (i) pristine MWNTs, (ii) MWNTs-*g*-(BCB)$_n$, 28 wt % BCB, (iii) MWNTs-*g*-(BCB-Br)$_n$, 35 wt % BCB-Br, (iv) MWNTs-*g*-(BCB-CH_2CH_2OH)$_n$, 47 wt % BCB-CH_2CH_2OH, and v) MWNTs-*g*-(BCB-DPE)$_n$, 54 wt % BCB-DEP. (b) Extent of functionalization depending on the reaction temperature and duration: (i) bulk reaction of BCB with MWNTs at different temperature for 24 h, and (ii) dropwise addition of BCB-CH_2CH_2OH at 235 °C for different duration

repeated several times until the filtrate showed the absence of BCB by thin-layer chromatography. Benzocyclobutenes containing hydroxyl (**4**) and 1-phenyl-1-benzocyclobutene ethylene (**5**) were reacted in tetradecane using dropwise addition. The side-wall-functionalized MWNTs (MWNTs-*g*-(BCB)$_n$) each having different substitution in BCB, **1**−**5**, were dried at 60 °C for 5 h under a vacuum and characterized using FT-IR, UV–vis absorption spectroscopy, Raman spectroscopy, and thermogravimetric analysis (TGA).

The quantity of BCBs attached to the surface of MWNTs-*g*-(BCB)$_n$ was determined from TGA, which showed two distinct weight losses: (i) starting from 200 to 480 °C and (ii) a major weight loss at 590−625 °C. The decompositions in the temperature ranges 200−480 °C and 590−625 °C were assigned to the attached BCBs and the MWNTs, respectively (Figure 1a). A different decomposition pattern was observed for **1**–**5** related to the nature of the substituted BCB. The TGA performed under N_2 showed presence of two steps of decomposition for the grafted BCB derivatives in the temperature range 200–480 °C. The amount of BCBs grafted to the tubes varies from 6 to 54 wt % depending on the reaction temperature as well as the mode of addition (Figure 1b).

As the reaction proceeds through the formation of *o*-quinodimethane radicals, the rate of Diels–Alder adduct formation is dependent on the temperature of the reaction. The control of the process is evident through an increase in weight percent of BCB on the surface of MWNTs with increasing reaction temperature in bulk (Figure 1b−i). At 140 °C, only 6.9 wt % BCB was grafted on the surface of the MWNTs. On the other hand, when the reaction was performed at 190 °C, the grafting of BCB increased up to 28.6 wt %. The reaction of 1-bromobenzocyclobutene (**2**) with MWNTs in bulk gave MWNTs-*g*-(BCB-Br)$_n$ with 35 wt % functionalization (Supporting Information). Similarly, another isomeric bromobenzocyclobutene (**3**) also gave 30 wt % functionalization determined by TGA. However, it was observed that a prolonged reaction time has no significant influence on the weight percent of grafting, which could be attributed to the dimerization of *o*-quinodimethane radical intermediate. For example, reaction of **1** and **3** with MWNTs performed in bulk for 8 and 24 h produced a similar weight percent functionalization. To minimize the dimerization of BCBs, we kept the substituted BCBs, **4** and **5**, at room temperature and added them dropwise into tetradecane-containing MWNTs at 235 °C.

The dropwise addition method significantly improves the percentage of grafting depending on the duration of the reaction. The reaction performed with **4** was kept stirring for 30, 90, and 100 min, and the TGA revealed that the weight percent decomposition of the substituted BCB increased from 29.2, 43.5, and 47.6 wt %, respectively. This indicates that the Diels–Alder reaction using BCB is controllable and the extent of grafting on to the surface of the MWNTs can be tailored using a suitable reaction temperature and time (Figure 1b−ii).

The FT-IR spectrum of the various substituted MWNTs-*g*-(BCB)$_n$ reveals characteristic vibrations of aromatic and CH modes (∼3010 and 2930 cm^{-1}, respectively) along with the characteristic vibration modes for the substitution group, confirming the presence of substituted BCB on the MWNTs (Supporting Information). The UV–vis absorption spectrum of **1** (Figure 2a−i) shows a broad absorption signal monotonously decreasing from 250 to 900 nm corresponding to the MWNTs. Similarly, MWNTs-*g*-(BCB-Br)$_n$ (**2**) also confirms the presence of MWNTs (Figure 2a-ii). The Raman spectra of these functionalized MWNTs are similar to the pristine MWNTs showing a characteristic tangential band at ∼1566 cm^{-1} and a disorder band at ∼1340 cm^{-1}. However, the ratio of these bands (I_d/I_t) is slightly high in the case of functionalized samples as compared to pristine MWNTs, indicating the introduction of sp^3 carbons on the surface of the MWNTs (Figure 2b).

Covalent functionalization of MWNTs with polymer using a grafting-to strategy is known in the literature.[2] It was expected that a polymer containing benzocyclobutene repeat units such as poly(4-vinyl benzocyclobutene) (PVBCB) would react at multiple sites on the surface of the MWNTs. If the proximity of the tubes permits, interlinking of MWNTs can be realized. The PVBCB was synthesized as reported elsewhere using anionic polymerization of 4-vinyl benzocyclobutene and reacted with MWNTs.[13] Accordingly, 20 mg of MWNTs was refluxed in 15 mL of diphenylether containing 20 mg of PVBCB ($M_{n,SEC}$ = 30000 g/mol, M_w/

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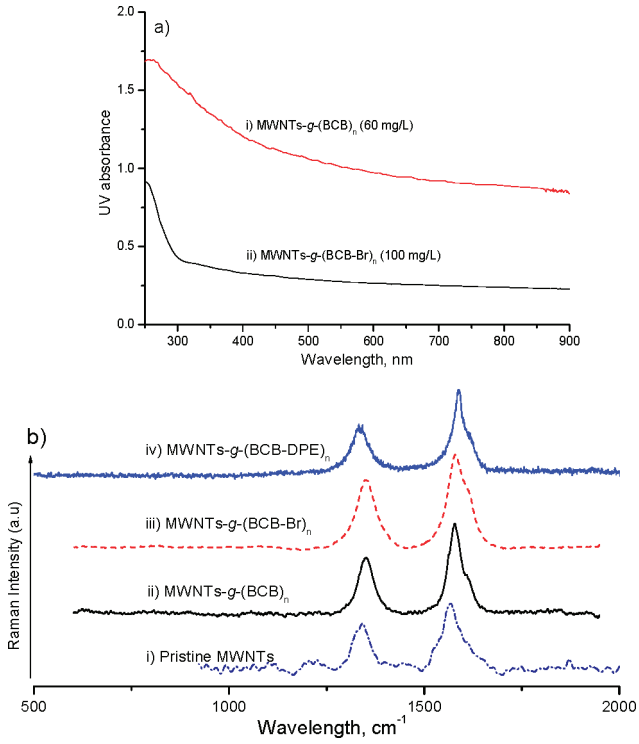

Figure 2. (a) UV–vis absorbance of benzocyclobutene-grafted MWNTs solutions in $CHCl_3$: (i) MWNTs-*g*-$(BCB)_n$ (60 mg/L, n = 28 wt %), and (ii) MWNTs-*g*-$(BCB\text{-}Br)_n$(100 mg/L, n = 35 wt %). (b) Raman spectra of various benzocyclobutene grafted MWNTs.

M_n = 1.05) at 240 °C for 2 h. After the reaction, the MWNTs-*g*-$(PVBCB)_n$ were washed with copious amount of tetrahydrofuran and recovered by filtration and dried at 90 °C for 4 h. The recovered MWNT-*g*-$(PVBCB)_n$ had a weight increase of 19 mg (95 wt %), indicating the total amount of PVBCB had undergone cross-linking via inter- or intramolecular reactions. The TGA of MWNTs-*g*-$(PVBCB)_n$ showed a 4% weight increase at 260 °C and 50% weight loss up to 500 °C corresponding to the grafted PVBCB on the MWNTs. The decomposition of MWNTs is clearly seen at 568 °C. The weight increase is attributed to the reaction of residual pendant BCB groups of the polymer with oxygen present in the furnace. This confirms that the BCB groups present in the polymer have partially undergone the grafting reaction with MWNTs (Supporting Information). It is also known that PVBCB undergoes intramolecular cross-linking to form organic nanoparticles.[14] The MWNTs-*g*-$(PVBCB)_n$ obtained was found soluble in THF and $CHCl_3$ at low concentration (Supporting Information).

The TEM analysis of a sample prepared by drop-coating a solution of MWNTs-*g*-$(PVBCB)_n$ on a carbon grid showed the presence of cross-linked organic polymer as nanoclusters on the surface of MWNTs (Figure 3). The nanoclusters on the surface of MWNTs are nonuniformly located on the surface, which could be attributed to a random heterogeneous Diels–Alder reaction of benzocyclobutene pendants of polymer with sp^2 carbons of the MWNTs. It appears that once the chemical anchoring of polymer occurs at sp^2 carbon of the MWNTs, the

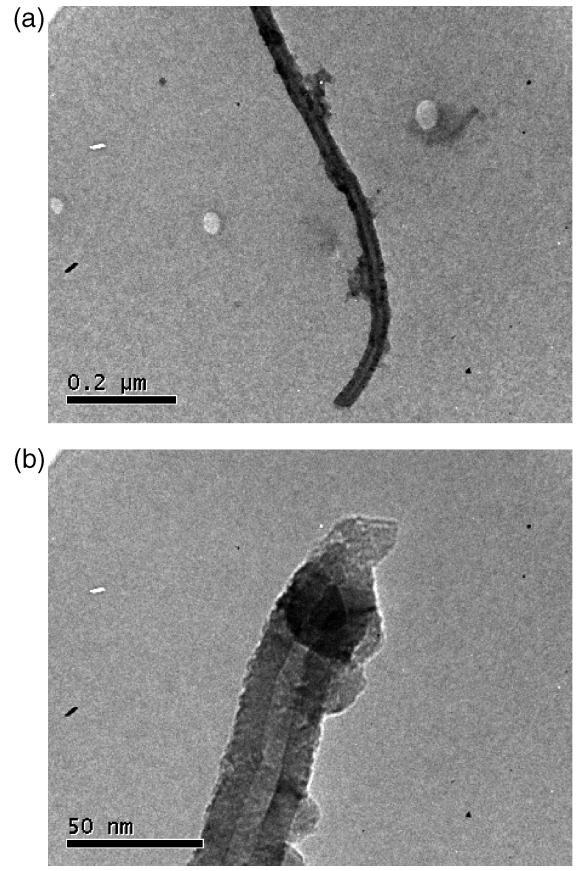

Figure 3. (a, b) Organic nanoclusters of cross-linked poly(4-vinylbenzocyclobutene) on the surface of MWNTs.

remaining tangling polymer chain undergoes inter- and intramolecular cross-linking reaction to form a collapsed polymeric nanocluster on the surface of the MWNTs. The size of nanocluster ranging from 5 to 13 nm also suggests that it involves reactions of intermolecular PVBCB on the surface of MWNTs. It is possible that by controlling the PVBCB chain-length or molecular weight, one can also control the size of added globs on the surface of MWNTs. The formation of polymeric nanoclusters on the surface of MWNTs through covalent cross-linking can be used to connect MWNTs to surfaces suseptible to radical intermediate.

In conclusion, we report a simple Diels–Alder reaction for the functionalization of MWNTs using benzocyclobutene. The extent of functionalization can be controlled by using the appropriate temperature and mode of addition of the reagent and by controlling the reaction duration. The use of polymer containing pendant benzocyclobutene produces cross-linked organic nanoclusters covalently connected to the surface of the MWNTs.

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Supporting Information Available: Experimental section and characterization details such as TGA of **1** and **2**, FT-IR of **4** and **5**, and more TEM (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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